VII SBIR, HBCU, & UCR Projects

VII.1 Bi-Layer p-n Junction Devices for Coal-Based SOFC Interconnections

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Objectives

- Develop a stable, high-conductivity bi-layer interconnection (IC) for lower operating temperature solid oxide fuel cells (SOFCs).

Approach

- Analyze and model a bi-layer IC comprising of a p-type and an n-type semiconducting layer using literature data for well-known materials.
- Develop design criteria for a bi-layer IC based on the model.
- Investigate techniques for fabricating a bi-layer IC.

Accomplishments

- Analyzed bi-layer IC structures using species transport models and developed design criteria for fabrication of such structures.
- Conducted preliminary investigations into fabricating bi-layer IC structures.

Future Directions

Future work in this project will focus on combining detailed measurement of partial conductivities of various p- and n-type oxides with a study of various fabrication techniques to identify the most appropriate technique to fabricate bi-layer ICs.

Introduction

Current research on solid oxide fuel cells (SOFCs) is focused on reducing the operating temperature from a nominal temperature of 1000°C to 600-800°C. Reducing the operating temperature allows the use of low-cost stack and manifolding materials, reduces heat-up time, and enables use in small-scale residential and transportation applications. However, reducing the operating temperature also has the unintended negative consequences of higher electrode polarization and higher area specific electrolyte and interconnection resistances. In particular, doped $LaCrO_3$, a high-temperature p-type semiconductor which is used as the interconnection material in state-of-the-art high-temperature SOFCs, is a very poor choice for an interconnection material in the 600-800°C temperature regime for two different reasons. First, the conduction mechanism in doped-$LaCrO_3$ is small polaron hopping, which is a thermally activated process. Thus, the p-type conductivity of this material decreases exponentially with decreasing temperature. Secondly, the interconnection material,

like the solid electrolyte in the SOFC, is exposed to highly oxidizing conditions on the cathodic side ($pO_2 = 0.21$ atm) and highly reducing conditions on the anode side (10^{-18} to 10^{-21} atm). Thus, a gradient in the electronic conductivity exists across the interconnect, with a high conductivity on the cathode side and poor conductivity on the anode side leading to an overall low average electronic conductivity across the interconnect. In this project, we are studying a novel concept for an improved SOFC interconnection structure with a high average conductivity across the entire thickness.

Approach

The approach being explored in the current project utilizes a bi-layer IC with a p-type layer (electronic conductivity proportional to $pO_2^{1/n}$) exposed to the cathode gas (air or oxygen) and an n-type layer (electronic conductivity proportional to $pO_2^{-1/n}$) exposed to anode gas (mixture of H_2, H_2O, CO and CO_2). By designing the thickness of the layers appropriately, one can in principle maintain thermodynamic stability of the layers while at the same time retaining a high average electronic conductivity across the IC.

Results

The principal result from Phase 1 of this project is a detailed analysis of a model bi-layer SOFC IC culminating in definitive design criteria for such a structure. The results have given a firm direction for future work in this area. The analysis of the bi-layer IC structure and the design criteria ensuing from the analysis are described in what follows.

Figure 1 shows a schematic of the bi-layer interconnection and associated transport directions of oxygen ions (O^{2-}), holes (h^+) and electrons (e^-). The generalized current density of species 'k' is given by

$$J_k = -\frac{\sigma_k}{z_k e} \nabla \eta_k \qquad (1)$$

Applying equation (1) to transport of O^{2-}, h^+, and e^-, the species current densities can be written as,

$$J_i = \frac{\sigma_i}{2e} \nabla \eta_i \qquad (2a)$$

$$J_p = -\frac{\sigma_p}{e} \nabla \eta_p \qquad (2b)$$

$$J_n = \frac{\sigma_n}{e} \nabla \eta_n \qquad (2c)$$

The sum of the species' current densities can then be equated to the total current density through the bi-layer interconnection under SOFC operating conditions, i.e.

$$J = J_i + J_p + J_n \qquad (3)$$

The next step in the analysis is the assumption that local thermodynamic equilibrium prevails between neutral oxygen gas, oxygen ions and electrons/holes, i.e. the following reactions are in thermodynamic equilibrium everywhere across the interconnection structure.

$$(1/2)O_2 + 2e^- = O^{2-} \qquad (i)$$

$$(1/2)O_2 = O^{2-} + 2h^+ \qquad (ii)$$

$$null = e^- + h^+ \qquad (iii)$$
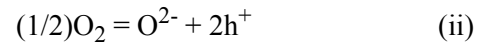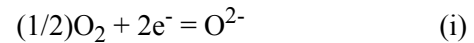
Assumption of thermodynamic equilibrium of the above reactions gives,

$$\frac{1}{2}\nabla\mu_{O_2} + 2\nabla\eta_n = \nabla\eta_i \qquad (4)$$

$$\frac{1}{2}\nabla\mu_{O_2} + 2\nabla\eta_n = \nabla\eta_i \qquad (5)$$

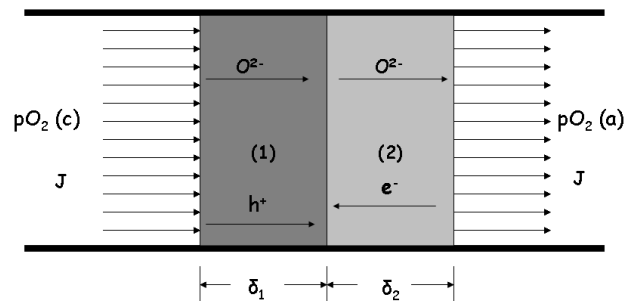$$\nabla\eta_n + \nabla\eta_p = 0 \qquad (6)$$

(1): p-type (2): n-type

Figure 1. Schematic of a Bi-layer IC

$$J_{el} = J_n + J_p = \frac{\sigma_n + \sigma_p}{\sigma_i + \sigma_n + \sigma_p} J - \frac{1}{2e} \frac{\sigma_i (\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p} \nabla \mu_{O_2} \quad (7a)$$

$$J_i = \frac{1}{2e} \frac{\sigma_i (\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p} \nabla \mu_{O_2} + \left(\frac{\sigma_i}{\sigma_i + \sigma_n + \sigma_p} \right) J \quad (7b)$$

Substituting equations (2), (4), (5) and (6) in (3), it can be shown that

Each of the above equations – (7a), which represents the total electronic current density (electron and hole current density), and (7b), which represents the total ionic current density – has two terms, one associated with *J*, the total external current density, and the other $\nabla \mu_{O_2}$, the neutral oxygen chemical potential gradient. The transport coefficient multiplying $\nabla \mu_{O_2}$, namely ,

$$\frac{\sigma_i (\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p}$$

is easily recognized as the ambipolar conductivity of the individual layers. In general, the conductivities σi, σ_n and σ_p will be functions of temperature and composition. Since the composition is both a function of the local electrostatic potential and the oxygen partial pressure, the conductivities are expected to vary as a function of position. Relevant simplifying assumptions to derive analytical expressions can now be made that can guide design of the bi-layer interconnection.

First, we assume that the ionic conductivity in the two layers is invariant with pO_2. Second, we assume that the ionic conductivity is much smaller in magnitude than the sum of the electron and hole conductivities, i.e. $\sigma_i << (\sigma_n + \sigma_p)$. The first assumption is true of most p-type and n-type oxide electronic conductors. In these materials, the oxygen ionic conductivity is determined extrinsically, i.e. it is a stronger function of the aliovalent dopant level than of pO_2. The second assumption is a necessary condition to be satisfied of any candidate interconnection material. With the second of these assumptions, equations (7) can be simplified to

$$J_{el} = J - \frac{1}{2e} \sigma_i \nabla \mu_{O_2} \quad (8a)$$

$$J_i = \frac{1}{2e} \sigma_i \nabla \mu_{O_2} \quad (8b)$$

These assumptions imply that at steady state, the current passing through the bi-layer interconnection is substantially electronic in nature. Furthermore, the rather small oxygen ionic current through the bi-layer given by equation (8b) does not depend on the total current through the interconnection but only on the cathodic and anodic side pO_2's. Assuming that the chemical and electrostatic potential gradients are one-dimensional and integrating equation (8b) over both layers, it can be shown that,

$$J_{i1} = \frac{k_B T \sigma_{i1}}{2e\delta_1} \ln\left[\frac{pO_2(c)}{pO_2(i)} \right] \quad (9a)$$

$$J_{i2} = \frac{k_B T \sigma_{i2}}{2e\delta_2} \ln\left[\frac{pO_2(i)}{pO_2(a)} \right] \quad (9b)$$

The interfacial oxygen partial pressure pO_2 *(i)*, which is an important design parameter as will be seen shortly, can be derived by equating the ionic current densities through the two layers at steady state, i.e. $J_{i1} = J_{i2}$, i.e. Equation (10) gives the

$$pO_2(i) = \left[\{pO_2(c)\}^{\left(\frac{\sigma_{i1}}{\delta_1}\right)} \{pO_2(a)\}^{\left(\frac{\sigma_{i2}}{\delta_2}\right)} \right]^{\frac{1}{\left(\frac{\sigma_{i1}}{\delta_1} + \frac{\sigma_{i2}}{\delta_2}\right)}} \quad (10)$$

interfacial oxygen partial pressure as a function of the oxygen partial pressure on the cathodic and anodic sides, the oxygen ionic conductivities in the two regions and the thickness of the two layers. The principal criterion is for pO_2 *(i)* to remain above the decomposition oxygen partial pressure for the p-type layer. Figure 2 shows as a function of p-type layer thickness for an assumed n-type layer thickness of 500 μm and SOFC operating temperature of 900°C, using literature data for two prototypical materials, namely, Sr-doped $LaMnO_3$ or LSM (p-type) and Y-doped $SrTiO_3$ or YST (n-type). Since LSM has a decomposition oxygen partial pressure of roughly 10^{-6} atm, it can be concluded for this configuration that the LSM layer thickness has to be about 5 μm. Figure 3 shows the variation of pO_2 as a function of
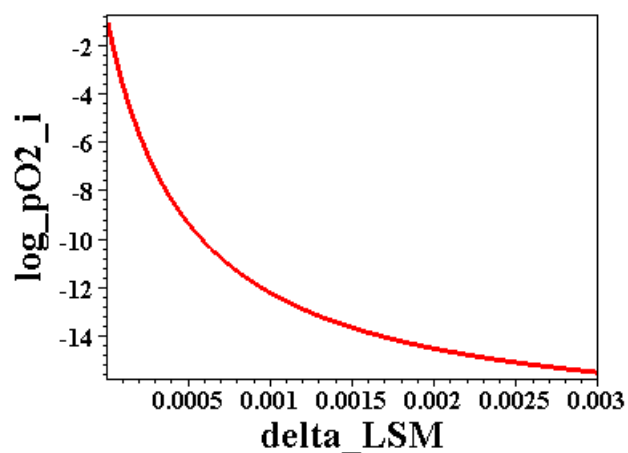
Figure 2. Variation of pO_2 in atm with varying LSM layer thickness in cm. Assumed fixed YST thickness is 500 microns. Ionic conductivity of YST is 10^{-5} S/cm and that of LSM is 10^{-7} S/cm; operating temperature is 900°C. Air side pO_2 is 0.21 atm and fuel side pO_2 is 10^{-18} atm.
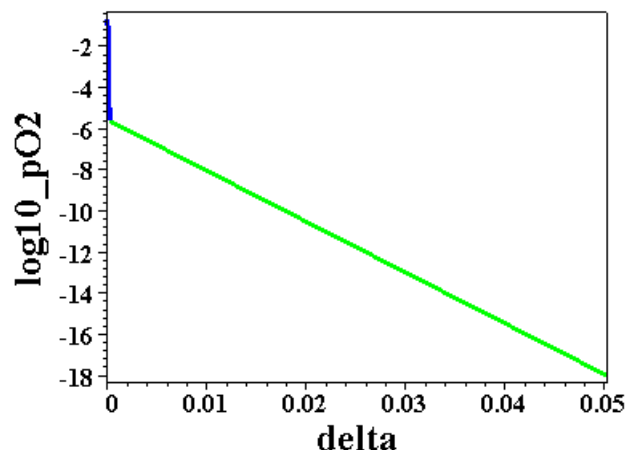

Figure 3. Variation of pO_2 across a bi-layer IC comprising a 5 micron thick LSM layer and 500 micron thick YST layer. Ionic conductivities of the layers and the air side and fuel side pO_2's are as in Figure 2.

position across the thickness for the same pair of materials and same operating conditions as in Figure 2.

Thus, a simple rule of thumb for design of the bi-layer IC is: ***the layer with the higher oxygen ionic conductivity has to be fabricated with a greater thickness.***
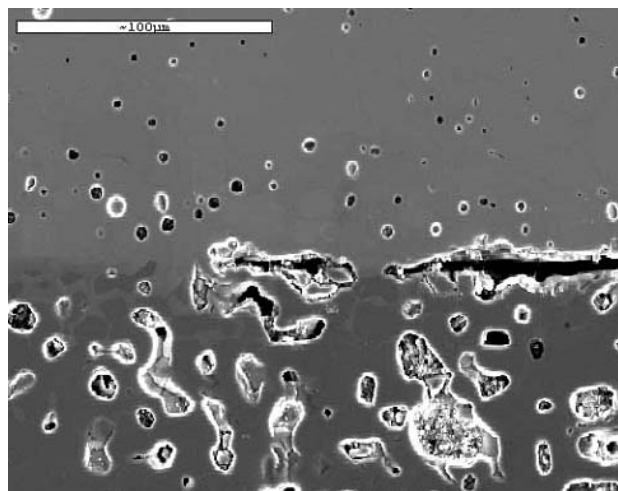

Figure 4. Micrograph of a bi-layer IC fabricated by contacting sintered pellets of LSM and YST at elevated temperature. Note the uneven bonding.

Similar design criteria can be developed for other pairs of materials if detailed partial conductivities of the p- and n-type materials are known as a function of temperature and pO_2.

Preliminary experiments have been performed to fabricate bi-layer structures by contacting sintered compacts of LSM and YST at elevated temperatures. Microstructures of the interface of bi-layers obtained using this method indicate discontinuous contact between the layers (Figure 4). Fabrication techniques including electrophoretic deposition, screen printing and thermal spray deposition are presently being investigated.

The focus of future work in this area will be:

- To obtain detailed partial conductivity data on various p-type and n-type perovskites as a function of pO_2 and temperature.

- To identify the most appropriate fabrication technique to fabricate bi-layer IC structures.

Conclusions

- Design criteria have been developed for design of bi-layer ICs.

- A general rule of thumb for bi-layer IC design is to fabricate the layer with the higher oxygen ion conductivity with a greater thickness.

References

1. A.V. Virkar, *J.Electrochem.Soc.*, (138) 5 (1991) 148

2. T. Kawada, T. Watanabe, A. Kaimai, K. Kawamura, Y. Nigara and J. Misuzaki, *Solid State Ionics,*108 (1998) 391

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FY 2004 Publications/Presentations

1. W. Huang and S. Gopalan, "Bi-layer Structures as SOFC Interconnections", *J.Power Sources* (Submitted)

2. W. Huang and S. Gopalan, "Bi-layer Interconnections for Coal Based Solid Oxide Fuel Cells (Innovative concepts – phase I), DOE UCR Contractors Review Meeting, Pittsburgh, PA, 6/19/04

3. W. Huang and S. Gopalan, "Bi-Layer Structures for Interconnections in SOFCs", to be presented in MRS Fall meeting, November 2004